

CHARACTERIZATION AND COD FRACTIONATION OF DOMESTIC WASTEWATERS

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Abstract

Results of a comprehensive study are reported for wastewater characterization in relation to modelling and design of biological nutrient removal systems for the Metropolitan Area of Istanbul. Domestic sewage quality was experimentally assessed in terms of major polluting parameters. Size distribution and calculation of significant ratios such as $BOD_5:COD$ and $COD:N$ were used to evaluate the merit of candidate physical, chemical and biological treatment alternatives. COD fractionation was effected to assess biological treatability and to yield the necessary process components to the recent modelling approaches.

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INTRODUCTION

In the past, domestic wastewater treatment was basically confined to organic carbon removal. In recent years, increasing pollution in the receiving waters and more stringent effluent limitations for discharges to sensitive zones have been the driving force in developing and implementing new treatment techniques to control, in addition to carbon, other significant parameters such as nitrogen, phosphorus, and priority pollutants. This new approach for wastewater management has greatly affected the concept of wastewater characterization.

The Istanbul Metropolitan Area is located on the northern shore of the Marmara Sea and lies on both sides of the Bosphorus connecting the Black Sea to the Marmara Sea. Recent studies indicate that water quality in the Marmara Sea gives severe indications of future, if not present, eutrophication problems, much in evidence by high nitrogen and phosphorus concentrations as well as the primary productivity levels in the upper layer (Orhon, 1995). Consequently, nutrient removal has been recently adopted as an integral part of the wastewater management plan for all discharges to the Marmara Sea, both in compliance with the related EEC directive, and to minimize nutrient discharges to the water body.

The Istanbul Metropolitan Area is the major polluter in the Marmara basin, currently housing a population of around 10 million and a significant portion of the

industrial activity in Turkey. In this context, an accurate assessment of the pollutant loads generated in the area is very important both for the selection and design of appropriate treatment technologies and for the evaluation of the impact produced on the adjacent receiving waters.

Furthermore, the technical description and the optimization of the nutrient removal scheme require a thorough understanding of the character of domestic sewage, both conventionally and in terms of new approaches involving COD fractionation and treatability oriented characterization.

This paper reports the first part of a comprehensive study carried out for the characterization of domestic sewage in relation to modelling and design of wastewater treatment processes for the Metropolitan Area of Istanbul. It summarizes a comparative evaluation of sewage quality from different parts of the area using different parameters and discusses expected impacts of the experimental assessment of sewage quality on the adopted wastewater management scheme.

MATERIALS AND METHODS

All analyses were performed as defined in Standard Methods (APHA, 1989). Evaluations of the characteristics of settled sewage were made on the supernatant of a cylindrical settling column after a holding time of 2 h. The soluble (filtered) COD was defined as the filtrate through Whatman GF/C glass fibre filters which were also used to assess SS and VSS parameters.

The readily biodegradable COD was measured in accordance with the method proposed by Ekama *et al.* (1986). The method relies on a respirometric procedure conducted on a 1-litre aerobic batch reactor fed with the sewage sample and seeded biomass to provide the required initial F:M ratio. Previous acclimation of biomass to the sewage sample tested was secured in a fill and draw reactor continuously operated at a sludge age of 7 days. Aliquots were removed from the reactor every 5–10 min for OUR measurements, conducted with a WTW OXI DIGI 2000 oxygen meter and recorder. The initial heterotrophic biomass in sewage was determined by a similar respirometric procedure without the initial seeding, as proposed by Henze (1986).

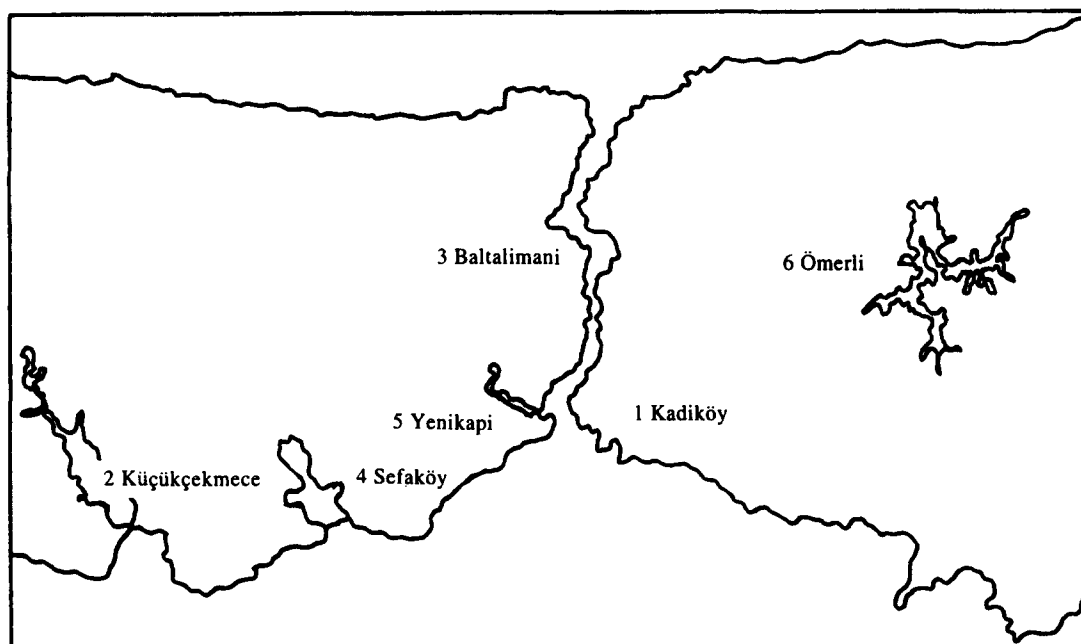


Fig. 1. Location of sampling stations in the Metropolitan Area of Istanbul.

The inert COD fractions were assessed using the methods defined by Orhon *et al.* (1994a). For the samples from station 1 (Kadıköy), the adopted procedure basically consisted of running two aerated batch reactors, one fed with raw and the other with filtered wastewater, and measuring the final threshold values of the total and soluble COD at the depletion of all biological activity. For the sample from station 5 (Yenikapı), the procedure was a modification of that previously proposed by Germirli *et al.* (1991) to assess S_I , involving three aerated batch reactors. The first two reactors were started with the initial total (C_{TO}) and soluble (S_{TO}) COD of the sample and the third reactor was fed with a glucose concentration adjusted to equal S_{TO} . In all the reactors the threshold soluble COD was measured after all the biodegradable COD was consumed. Both procedures also define the necessary calculations to separately assess S_I and X_I .

DESCRIPTION OF THE STUDY AREA

The study was conducted on wastewaters generated within the Metropolitan Area of Istanbul. The city serves as the perfect site for a characterization survey, extending over a wide area on the Asian and the European sides of the Bosphorus along the coast of the Marmara Sea, housing a population of around 10 million and more than 40% of the industrial activity in Turkey.

A complete network of sewers collects wastewaters at 15 different treatment and discharge points. In 1990, the total wastewater discharge was estimated as $15.5 \text{ m}^3 \text{ s}^{-1}$ with a potential daily pollution load of 335 tons of BOD_5 , 54 tons of nitrogen and 9 tons of phosphorus (Orhon *et al.*, 1994b).

Conventional characterization was performed on statistically significant numbers (i.e. more than 30 samples) of daily composite wastewater samples collected over a period of two years from six different stations. Locations of these sampling points are indicated in Fig. 1. Emphasis was placed on Kadıköy station (station 1), mainly because it reflects the largest sewage collection zone, representing 24% of the pollution flow and load of the city. Similar surveys were also conducted on samples taken from Küçükçekmece (station 2) and Baltalimani (station 3) stations located on the coast of the Marmara Sea and the Bosphorus, respectively. These three stations had the common feature of representing domestic sewage as they are practically unaffected by industrial wastewater discharges. The other three stations were mainly included in the study for the purpose of comparative evaluation, as they were expected to yield wastewater samples of significantly different character: wastewater at the Sefaköy station (station 4) was heavily affected by a number of different industrial activities. During the study period, the Yenikapı station (station 5) was considered to be the collection point of the wastewaters from the largest tanneries complex in the city, together with those from a sizeable residential and commercial community. Finally, the Ömerli station (station 6) represented a low-cost housing area where the wastewater flows were significantly affected by shortages in water supply.

CONVENTIONAL CHARACTERIZATION

Experimental results

Experimental results on conventional characterization of wastewaters are outlined in Table 1. The major observation was that the mean values of significant

Table 1. Conventional characterization of municipal wastewater in Istanbul

Parameter (mg litre ⁻¹)	1 (Kadıköy)		2 (Küçükçekmece)		3 (Baltalimanı)		4 (Sefaköy)		5 (Yenikapı ^a)		6 (Ömerli)	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
COD	220-775	450	345-480	400	265-645	340	750-6500	3750	280-1480	680	700-1600	1000
BOD ₅	150-410	220	160-210	185	73-200	150	200-1700	880	110-425	300	315-680	460
TKN	22-73	49	38.6-46.7	42	23.9-57	35	11.4-22.7	21	27-92	66	81-165	98
NH ₃ -N	25-39	30.5	22.4-30.4	24.78	10-26.3	19.9	3.8-7.3	4.77	24-48.8	37.74	—	—
Nitrite	—	—	0.005-0.17	0.049	0.005-0.112	0.051	0.035-0.4	0.195	—	—	<0.005-0.112	0.03
Nitrate	—	—	0.07-0.84	0.27	0.042-3.17	0.67	0.95-1.75	1.478	—	—	<0.005	<0.05
TP	5.0-1.5	8.1	6.1-9.6	7.4	5-8.63	6.8	45-320	220	3.6-13	7	13-32	18.5
Ortho-phosphate	—	—	2.9-4.3	3.3	2.15-3.2	2.62	8.4-60	25.73	—	—	—	—
SS	140-930	3.10	165-270	200	85-318	140	160-900	630	110-820	480	250-755	460
VSS	130-395	210	100-105	103	120-135	125	—	—	65-69	65	170-690	390
TSM	425-495	474	520-680	616	335-537	435	1830-4650	3431	—	—	—	—
Alkalinity	90-400	310	315-350	330	200-220	210	160-970	440	190-230	215	320-550	370
Oil and grease	62-135	84	180-230	206	110-155	124	210-450	281	137-150	146	—	—
Chloride	85-115	96.2	115-120	116.4	85-90	90	250-840	513	650-1500	1039	—	—
Detergent	2.45-4.1	3.2	3.5-4.15	3.81	3.75-4.4	4.12	160-760	494	1.3-2.98	1.68	—	—
pH	—	7.2	7.6-7.7	7.68	7.2-7.5	7.4	6.8-11.1	7.93	7.1-7.3	7.24	7.0-7.5	7.3
Phenol	0.26-0.64	0.52	0.04-1.48	0.41	0.056-0.136	0.08	0.03-0.65	1.143	0.7-1.0	0.77	—	—
Sulphide	1.7-3.04	2.37	—	—	<1.0-1.6	1.1	—	—	—	—	—	—
Pb	0.04-0.15	0.07	0-<0.5	<0.5	<0.2-<0.5	<0.3	—	—	—	—	—	—
Zn	0.15-0.3	0.26	03-0.7	0.54	0.17-1.46	0.38	—	—	0.3-1.7	0.8	—	—
Cu	0.04-0.07	0.05	0-<0.1	<0.1	<0.1-0.63	0.1	<0.1-<0.15	<0.1	—	—	—	—
Ni	0.03-0.07	0.04	—	—	—	—	0-<0.15	<0.15	—	—	—	—
Cr	0.005-0.05	0.02	—	—	<0.1-0.17	<0.1	0.1-1.1	0.4	0.5-1.75	1.0	—	—
Cd	—	—	<0.05-0.12	<0.05	<0.02-0.05	<0.03	<0.05-0.06	<0.05	0-<0.1	<0.1	—	—

^aWith the tannery discharges.

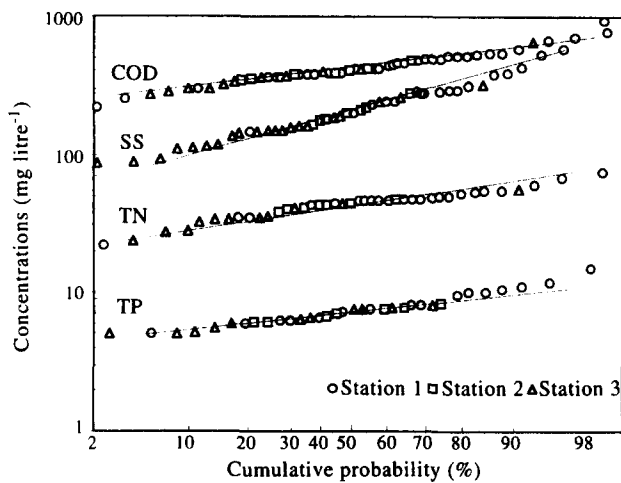


Fig. 2. Statistical distribution of COD, SS, total N and total P for stations 1, 2 and 3.

parameters were in close agreement for stations 1, 2 and 3, assumedly representing residential areas generating sewage without significant impact of industrial activities. A combined evaluation of the analyses related to these three stations was also performed as shown in Fig. 2, to yield an overall domestic sewage quality for Istanbul. The new values resulting from this evaluation were calculated as $410 \text{ mg litre}^{-1}$ for COD, $180 \text{ mg litre}^{-1}$ for BOD_5 , $210 \text{ mg litre}^{-1}$ for SS, 43 mg litre^{-1} for TKN and $7.2 \text{ mg litre}^{-1}$ for total P.

The character of the wastewater at station 1, which served as the focal point of the study, was slightly stronger in terms of the organic content reflected by COD and BOD_5 concentrations of $450 \text{ mg litre}^{-1}$ and $220 \text{ mg litre}^{-1}$, respectively. These results agreed well with the assumptions of $40 \text{ g BOD}_5 \text{ capita}^{-1} \text{ day}^{-1}$, $45 \text{ g SS capita}^{-1} \text{ day}^{-1}$, $6.7 \text{ g TKN capita}^{-1} \text{ day}^{-1}$, and $1.3 \text{ g total P capita}^{-1} \text{ day}^{-1}$, together with a unit wastewater flow rate of $160 \text{ litre capita}^{-1} \text{ day}^{-1}$, previously used for the evaluation of the total pollution load of the Metropolitan Area of Istanbul (Orhon, 1995).

Characterization of municipal wastewaters has been the subject, or the indispensable starting point, of many studies. Table 2 gives a collection of selected results and provides an indication of how sewage quality is site-specific and varies from one location to another. It also shows that the mean results associated with Istanbul reflect a typical medium domestic wastewater quality. Aside from major parameters, the mean chloride content of the samples analysed was lower than $100 \text{ mg litre}^{-1}$, due to the fact that surface water sources serve for the Istanbul water supply. The total heavy metal content was observed to stay lower than $1.0 \text{ mg litre}^{-1}$, also confirming that the input of toxic industrial wastewater in these areas was practically negligible.

Analytical results associate a much stronger quality with the wastewaters at the other stations. The mean COD concentrations were calculated as $3750 \text{ mg litre}^{-1}$, $680 \text{ mg litre}^{-1}$ and $1000 \text{ mg litre}^{-1}$ for stations 4, 5 and 6, respectively. The very high detergent concentrations

in the range of $160\text{--}760 \text{ mg litre}^{-1}$ provided strong proof of the effect of various major industrial effluents at station 4. Similarly, the mean chloride concentration in excess of $1000 \text{ mg litre}^{-1}$ was basically due to tanneries responsible for a significant fraction of the wastewaters collected at station 5. The strong sewage character depicted at station 6 was however not related to industrial activity and could be explained on the basis of the relatively low water consumption in the surrounding low-cost residential community, mainly due to the inadequacy of the local water supply in the area.

The impact of industrial effluents on the wastewater quality in Istanbul is best illustrated by means of the investigation at station 5 (Yenikapı). In the last few years, the majority of the tanneries discharging to this station have been forced to move to a new location at the Asian side of the city. The wastewater survey has been extended beyond this period to explore the new wastewater composition without the tannery discharges. The results obtained are outlined in Table 3, giving a clear indication of the substantial decrease in the values of major parameters after the relocation of the tanneries. It is also interesting to note that the new wastewater character at this station matches well with the overall domestic sewage quality, previously defined for the Metropolitan Area, on the basis of measurements at the first three stations.

The size distribution of pollutants is a significant index of wastewater treatability. It may be used to assess the relative merit of physical, chemical or biological processes in removing different wastewater components. In this study, the size distributions of pollutants were evaluated in three groups defining the settleable, suspended and soluble portions of major parameters. The separation of settleable and suspended parts was done by plain settling, and glass fibre filters with an effective pore size of $1.3 \mu\text{m}$ were used to differentiate the soluble (filterable) fractions from the suspended fractions, as routinely done in general wastewater analyses. Experimental results related to stations 1, 2 and 3, used to characterize the domestic sewage quality of the study area, are summarized in Table 4, exhibiting the same type of general accord previously observed on samples from these stations. The soluble fraction was calculated to stay around 35% of the total COD on an overall basis. The overall ratio for the soluble BOD_5 fraction was practically the same as COD, varying however in the range of 29–42% among the stations, probably due to the more delicate nature of the BOD measurements. Similarly, the non-settleable portions of the overall COD and BOD_5 concentrations were evaluated as 73% and 80%, respectively. Measurements for TKN, TP, SS and VSS parameters were only performed for station 1. They showed that the majority of the TKN content was soluble, because of the ammonia and the soluble organic nitrogen fractions, and only 56% of the mean total P concentration was soluble. They further indicated that 63% of the SS and 53% of the VSS content were likely to be removed by plain settling.

Table 2. Quality of municipal wastewater in selected studies

	Total COD (mg litre ⁻¹)	Soluble COD (mg litre ⁻¹)	Total BOD ₅ (mg litre ⁻¹)	Soluble BOD ₅ (mg litre ⁻¹)	SS (mg litre ⁻¹)	VSS (mg litre ⁻¹)	TKN (mg litre ⁻¹)	NH ₃ -N (mg litre ⁻¹)	Total P (mg litre ⁻¹)	Alkalinity (mg litre ⁻¹)	Sulphate (mg litre ⁻¹)
(Pretorius, 1971)	500	178	—	—	252	217	—	25.4	6.4	—	—
(Kobayashi <i>et al.</i> , 1983)	288	—	163	—	118	98	—	33	3	225	—
(Barbosa & Santanna, 1989)	627	157	357	94	376	297	54	30	9.9	198	124
(Sanz & Polanco, 1990)	475	260	325	—	190	155	30	14	25	200	155
(Sanz & Polanco, 1990)	160	390	480	—	285	230	43	19	44	265	200
(Garuti <i>et al.</i> , 1992)	585	170	—	—	321	238	88	52.7	10.3	—	110
(Andreadakis, 1992)	—	—	259	—	—	—	—	39.3	5.9	—	—
(Andreadakis, 1992)	—	—	226	—	—	—	—	37.6	5.65	—	—
(Andreadakis, 1992)	—	—	198	—	—	—	—	33	4.95	—	—
(Chudoba & Pannier, 1994)	500	350	200	—	150	75	55	—	—	—	—
(Eliosov & Argamon, 1995)	635	205	201	92	356	249	43	40	—	—	—
(Chavez-Mejia & Jimenez-Cisneros, 1996)	416	270	149	—	155	67	57.4	44	9.3	709	—
This study	410	140	180	68	210	195	43	30	7.2	300	—

Table 3. The effect of tannery effluents on sewage quality at station 5 (Himmetoğlu, 1995)

Parameter (mg litre ⁻¹)	With the tannery discharges 1991		Without the tannery discharges 1994—95	
	Range	Mean	Range	Mean
COD	280-1480	680	300-635	470
BOD ₅	110-425	300	100-290	168
SS	110-820	480	110-664	310
TN	27-92	66	28-72	52
TP	3.6-13	7	2.75-6.80	5.2

Table 4. Conventional characterization at stations 1, 2 and 3

Parameter (mg litre ⁻¹)	1 (Kadıköy)			2 (Küçükçekmece)			3 (Baltalıman)			Overall		
	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD	
COD	Total	450	110	220-775	400	38	345-480	340	55	265-645	410	110
	Settled	300	60	230-525	—	—	—	—	—	—	300	60
	Soluble	155	35	93-210	145	13	135-165	120	13	85-125	140	30
BOD ₅	Total	220	43	150-410	185	15	160-220	150	43	73-200	180	42
	Settled	145	33	100-200	—	—	—	—	—	—	145	33
	Soluble	64	12	43-170	78	5	70-85	55	8	45-65	68	14
TKN	Total	49	9	22-73	42	2.5	38.5-47	35	8	24-57	43	8.5
	Settled	45	8	18-64	—	—	—	—	—	—	4.1	7.5
	Soluble	38	8	8-57	—	—	—	—	—	—	38	7.5
TP	Total	8	3	5-15	7.4	1.1	6.1-9.6	6.8	1	5-8.5	7.2	2
	Settled	6	2.5	4.5-14.5	—	—	—	—	—	—	6	2-5
	Soluble	4.5	2	2.2-10	—	—	—	—	—	—	4.5	2
SS	Total	310	105	140-930	200	25	165-270	140	50	85-318	210	105
	Settled	115	15	95-132	—	—	—	—	—	—	115	15
VSS	Total	210	50	130-395	103	4	100-105	125	13	120-135	145	38
	Settled	98	13	75-120	—	—	—	—	—	—	98	13

Table 5. BOD₅: COD ratios at all stations

Station	Total BOD ₅ :COD			Settled BOD ₅ :COD			Soluble BOD ₅ :COD		
	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range
1 (Kadıköy)	0.49	0.05	0.41-0.63	0.50	0.075	0.38-0.56	0.47	0.02	0.38-0.67
2 (Küçükçekmece)	0.48	0.05	0.42-0.57	—	—	—	0.52	0.03	0.47-0.55
3 (Baltalıman)	0.45	0.045	0.18-0.55	—	—	—	0.46	0.10	0.3-0.65
Overall (1, 2 and 3)	0.47	0.045	0.18-0.63	0.5	0.075 ^a	0.38-0.56	0.5	0.045	0.3-0.65
4 (Sefaköy)	0.26	0.0625	0.138-0.37	—	—	—	0.205	0.09	0.14-0.44
5 (Yenikapı)	0.44	0.105	0.16-0.70	0.44	0.165	0.31-0.68	0.55	0.195	0.21-0.81
6 (Ömerli)	0.44	0.045	0.39-0.54	0.5	0.035	0.45-0.56	0.5	0.265	0.3-0.88

^aMeasured only at Kadıköy/Riva.

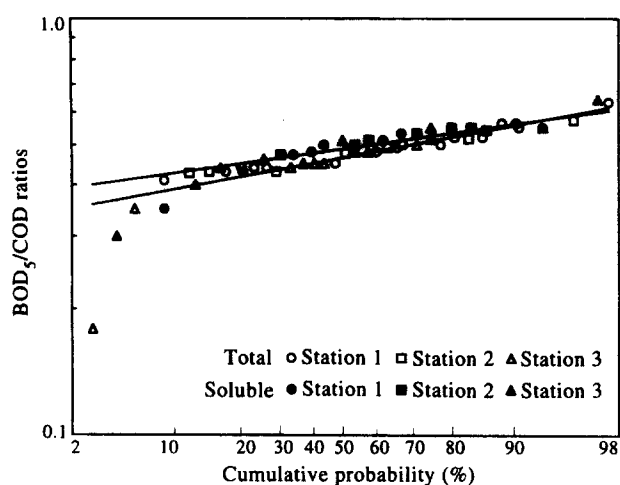


Fig. 3. Statistical distribution of BOD₅:COD ratios for stations 1, 2 and 3.

Assessment of significant parameters

Results of conventional characterization may be interpreted to yield, to a degree, a rough indication of the treatability of wastewaters. The BOD₅:COD ratio is a good example of such an interpretation. Both parameters are used as indices of the organic content of wastewaters; COD is a useful parameter for the modelling of biological kinetics as it sets electron equivalence of the substrate, biomass and oxygen requirement, but it reflects also biodegradable organics and residual components; BOD₅ is now regarded as a poor index of relatively easily biodegradable substrate. Consequently, BOD₅:COD ratio may be conceived as an acceptable index of biological treatability, or more accurately a rough proportion of easily and slowly biodegradable organic matter. For conventional wastewaters, such as domestic sewage, this ratio may be compared to f , BOD₅:BOD_u, traditionally associated with a value of 0.67–0.70, exhibiting however a much wider range in practice. Arceivala (1981) reports f values between 0.52 and 0.62 for domestic wastewater. In the USA, typical compositions for weak, medium and strong domestic wastewaters correspond to a range of 0.40–0.44 for this ratio (Metcalf & Eddy Inc., 1991). In Germany, however, a high value of 0.7 g BOD₅ g⁻¹ biodegradable COD is implicit in the assumptions used for the calculation of the biochemical oxygen requirements (Anon., 1991). The BOD₅:COD ratios calculated

for all the experimental stations included in this study are outlined in Table 5 and plotted in Fig. 3. The results indicated that the mean value of this ratio was 0.47 for all stations depicting domestic sewage character and remained about the same for the settled and soluble sewage fractions. It is worth noting that BOD₅:COD was observed to drop from 0.44 to 0.35 for station 5 (Yenikapı) after relocation of the tanneries, explainable by the fact that tannery wastewaters contain a higher level of easily biodegradable substrate as compared to domestic sewage. The heavy industrial character of wastewaters at station 4 (Sefaköy) was confirmed by a relatively low value of 0.26 for this ratio. Other significant outputs of the experimental results are the COD:N and the BOD₅:N ratios. They are especially important for the modelling and design of nitrification/denitrification systems. Traditionally, the influent BOD₅:N ratio is considered one of the critical factors for nitrification; if BOD₅:N < 4, nitrification is viewed as a separate process for domestic sewage; a value higher than this implies the adoption of a combined process. Similarly, the COD:N ratio is a parameter closely related to the denitrification potential of the wastewater, with different implications for pre- and post-denitrification systems. It plays a decisive role in the performance of biological nitrogen systems, especially in sensitive areas with high fluctuations in sewage quality and quantity (Görgün *et al.*, 1995; Artan *et al.*, 1995). In this study, the COD:N ratios for all the stations investigated were calculated as listed in Table 6 and illustrated in Fig. 4. It is noted that all experimental results exhibited a close agreement around a mean overall COD:N value of 9.2, again, with the exception of station 5 (Yenikapı), due to very strong industrial effluents devoid of nitrogen. The observed overall COD:N ratio was practically the same as the limit value of 10 below which single predenitrification has the potential to provide the highest denitrification efficiency (Orhon & Artan, 1994). The mean value of this parameter dropped to 6.5 and to 3.6 for the settled and filtered portions of wastewater samples analysed. Similarly, the means of the evaluations for the BOD₅:N ratio accumulated around an overall value of 4.3 characterizing the Istanbul domestic sewage, as shown in Table 7. In a manner similar to the COD:N ratio, this value exhibited a decrease to 3.25 and 1.7 for settled and filtered sewage fractions, respectively.

Table 6. COD:N ratios at all stations

Station	Total COD:N			Settled COD:N			Soluble COD:N		
	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range
1 (Kadıköy)	9	1.45	63–31.8	6.5	1.15	4.8–23.9	3.6	0.6	2.4–21.3
2 (Baltalımanı)	9.8	1.1	7.2–15.4	—	—	—	—	—	—
3 (Küçükçekmece)	9	0.9	7.78–10.3	—	—	—	—	—	—
Overall (1, 2 and 3)	9.2	1.65	6.3–31.8	6.5 ^a	1.15 ^a	4.8 ^a –23.9 ^a	3.6 ^a	0.6 ^a	2.4 ^a –21.3 ^a
4 (Sefaköy)	180	30	66–293	7.8	1.55	5.88–13.7	5.8	2	3.84–26.6
5 (Yenikapı)	10.5	1.4	6.85–21	—	—	—	—	—	—
6 (Ömerli)	9.8	1.95	6.67–14.4	7.4	1.4	5.6–8.89	4.5	0.85	3.43–5.79

^aMeasured only at Kadıköy/Riva.

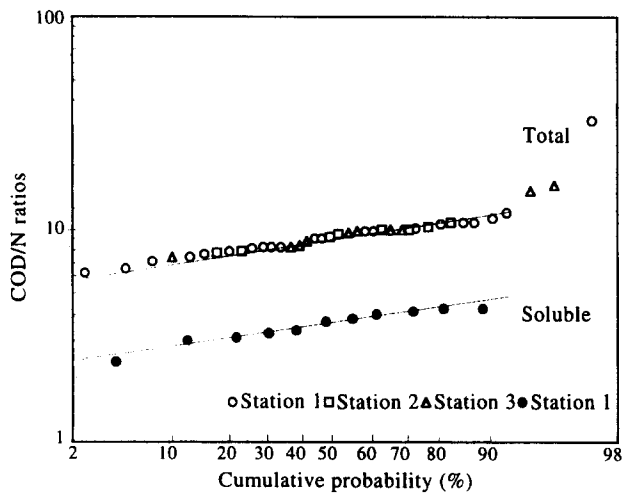


Fig. 4. Statistical distribution of COD:N ratios for stations 1, 2 and 3.

The fixed solids or the inert fraction of the suspended solids is implicit in the VSS:SS ratio of wastewaters. As shown in Table 8, this ratio was found to vary in the range of 0.48–0.8, around a mean value of 0.7 for stations reflecting domestic sewage quality, indicating that 30% of the suspended solids are of non-biodegradable nature. Figure 5 gives the statistical variation of this ratio and the observed increase from 0.68 in the raw sewage to 0.76 in the settled fraction, calculated for station 1. This parameter was observed to drop to a very low value of 0.175 for station 5, due to the effect of tannery discharges.

Evaluation of results

A reliable wastewater characterization is a prerequisite for an accurate assessment of the pollution load generated

from the Metropolitan Area of Istanbul, as well as the design of the appropriate treatment technologies. However, this issue was neglected in numerous related engineering studies conducted over the last 25 years. In these studies, sewage quantity and quality were routinely calculated on the basis of general unit values adopted from similar practices abroad, without any local experimental support. Table 9 and Table 10 give an overview of the sequence of unit wastewater flow rates and unit emission rates for major parameters proposed as part of the wastewater management strategies for Istanbul (Orhon, 1995). They generally reflect European or US practice as illustrated by the typical value of 60 g BOD₅ capita⁻¹ day⁻¹.

The interpretation of the proposed values in terms of resulting concentrations of major parameters is given in Table 11, together with corresponding percentile values of the concentration distribution profiles derived from the experimental data of this study. Table 11 also includes mean levels of the same parameters similarly calculated from the same experimental distribution profiles. As shown in this table, almost all proposed parameters exhibit a common feature of being too high and conservative beyond acceptable limits. In fact, a unit BOD₅ emission of 60 g capita⁻¹ day⁻¹ corresponds to a BOD₅ concentration of 375 mg litre⁻¹, a level which has never been reached in all the analyses conducted on Istanbul sewage. Consequently, concentrations of 250 mg litre⁻¹ BOD₅, 280 mg litre⁻¹ SS, 42 mg litre⁻¹ TKN and 8 mg litre⁻¹ total P were proposed as a result of existing experimental findings at that time for the calculation of pollution loads generated in the Metropolitan Area of Istanbul as of 1990 (Meriç, 1990; Orhon, 1995). However, such evidence did not stop

Table 7. BOD₅:N ratios at all stations

Station	Total BOD ₅ :N			Settled BOD ₅ :N			Soluble BOD ₅ :N		
	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range
1 (Kadıköy)	4.5	0.5	3.1–6.07	3.25	0.1	2.5–3.91	1.7	0.225	1.4–2.05
2 (Baltalimanı)	4.2	0.7	2.61–5.8	—	—	—	—	—	—
3 (Küçükçekmece)	4.3	0.55	3.78–5.18	—	—	—	—	—	—
Overall (1, 2 and 3)	4.3	0.675	2.61–6.07	3.25 ^a	0.1 ^a	2.5 ^a –3.9 ^a	1.7 ^a	0.225 ^a	1.4 ^a –2.04 ^a
4 (Sefaköy)	4.3	16.5	17.5–74.8	—	—	—	—	—	—
5 (Yenikapı)	4.5	0.8	3.38–5.56	4.1	0.95	2.33–5.18	3.7	0.85	2.98–21.67
6 (Ömerli)	4.6	1.1	3.04–6.1	3.5	0.8	2.55–4.51	2.35	0.68	1.5–3.51

^aMeasured only at Kadıköy/Riva.

Table 8. VSS:SS ratios at all stations

Station	Total VSS:SS			Settled VSS:SS		
	Mean	SD	Range	Mean	SD	Range
1 (Kadıköy)	0.68	0.1	0.32–0.93	0.76	0.15	0.42–0.95
2 (Baltalimanı)	0.8	0.12	0.75–0.9	—	—	—
3 (Küçükçekmece)	0.48	0.015	0.48–0.5	—	—	—
Overall (1, 2 and 3)	0.7	0.2	0.32–0.93	0.76 ^a	0.15 ^a	0.42 ^a –0.95 ^a
4 (Sefaköy)	—	—	—	—	—	—
5 (Yenikapı)	0.175	0.025	0.15–0.19	—	—	—
6 (Ömerli)	0.84	0.02	0.68–0.91	0.95	0.06	0.91–0.98

^aMeasured only at Kadıköy/Riva.

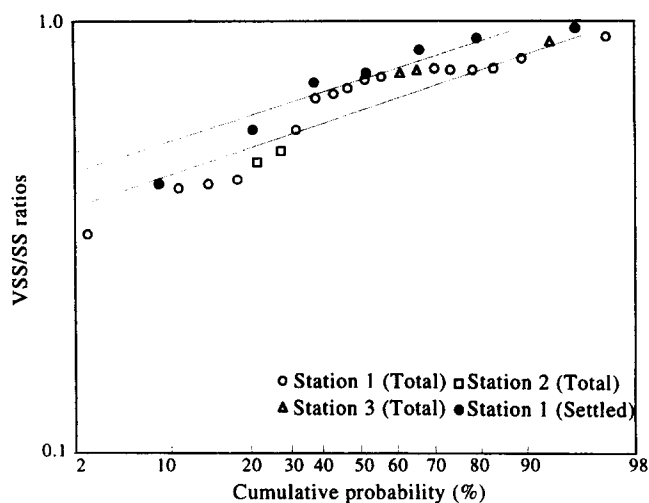


Fig. 5. Statistical distribution of VSS:SS ratios for stations 1, 2 and 3.

subsequent studies coming up with even higher and unrealistic values, as shown in Table 11 (IMC, 1994). Nevertheless, the experimental evidence put forward by this investigation formed the scientific basis of 200 mg litre⁻¹ BOD₅, 400 mg litre⁻¹ COD, 45 mg litre⁻¹ TKN and 7 mg litre⁻¹ total P, accepted as typical values for domestic sewage in major residential areas in Turkey, in the context of the recent national action plan for wastewater management, prepared by Orhon *et al.* (1995).

COD FRACTIONATION

Optimal design of biological treatment for domestic wastewaters now requires a thorough evaluation of system behaviour by means of mathematical modelling. Such models are only reliable if they are structured

Table 9. Adopted unit wastewater generation rates

Year	Unit Emission Rates, (litre capita ⁻¹ day ⁻¹)						
	DAMOC (1971)	Camp-Tekser (1975)	WMT (1986)	TBP & UBM (1991)	BWB (1991)	GWE & SP (1991)	Meriç (1990) IMC (1994)
1985	180 ^a (120–260)						
1990		130–220 ^b	160		160	160	169 ^a (144–239)
2000			200	200			171 ^a (159–264)
2020	265 ^a (230–294)	215–290 ^b	250	250	180	220	200 ^a (178–276)
2040							234 ^a (222–276)

^aMean value—100% of net water consumption.

^bVaried according to district.

Table 10. Adapted unit emission rates for major parameters

Parameter	Year	Unit Emission Rates, (g capita ⁻¹ day ⁻¹)						
		Camp-Tekser (1975)	WMT (1986)	TBP & UBM (1991)	BWB (1991)	GWE & SP (1991)	Meriç (1990)	IMC (1994)
BOD ₅	1990	50	60		60		40	60
	2020	75	60	60	70	60		70
	2040			70				80
SS	1990	75	70				45	70
	2020	105	70	70		70		90
	2040							105
Total N	1990	8	10		6.7		6.7	10
	2020	9	10	10		10		11
	2040							12
Total P	1990	2	2		1.3		1.3	2
	2020	2.5	2	2		2		2
	2040							2

Table 11. Comparison of measured concentrations with proposed values

	Measured mean concentration (mg litre ⁻¹)	Camp-Tekser (1975) (mg litre ⁻¹)	WMT (1986) (mg litre ⁻¹)	Meriç (1990) (mg litre ⁻¹)	IMC (1994) (mg litre ⁻¹)	DHI (1994) (mg litre ⁻¹)
		Percentile	Percentile	Percentile	Percentile	Percentile
COD	410	—	—	—	—	400
BOD ₅	180	285	375	250	355	200
SS	205	428	438	280	414	—
Total N	43	46	62.5	41.8	59	45
Total P	7.2	11.5	12.5	8.1	11.8	7

upon meaningful process components of substrate and biomass. The overall or total COD, although a convenient parameter, cannot be regarded as a valid process component in recent models for carbon and nutrient removal, because it covers, as illustrated in Fig. 6, a large spectrum of organic compounds with different biodegradation characteristics as well as inert components of influent origin or generated during biological treatment as residual microbial products. Consequently, wastewater characterization, if conceived as a useful tool to supply the necessary information for process modelling, should include COD fractionation as well as the assessment of conventional polluting parameters.

The commonly adopted approach today is to evaluate the total biodegradable COD (C_S) as two major components of readily biodegradable COD (S_S) and slowly biodegradable COD (X_S) in accordance with the original bi-substrate model proposed by Dold *et al.* (1980). These components may conveniently be expressed as fractions of the total COD (C_T):

$$S_S = f_{SS}C_T$$

$$X_S = f_{XS}C_T$$

Similarly, the total biodegradable COD may be defined as:

$$C_S = (f_{SS} + f_{XS})C_T = f_S C_T$$

where

f_{SS} = readily biodegradable fraction of the influent COD
 f_{XS} = slowly biodegradable fraction of the influent COD

and

f_S = total biodegradable fraction of the influent COD.

Evidently, both components are likely to contain a number of organics with a range of biodegradation rates, but this range is of no practical importance when compared with the rates separating these two groups (Dold & Marais, 1986). The distinctive feature of the readily biodegradable COD is that it can be directly absorbed for synthesis, whereas hydrolysis is required first for the utilization of the slowly biodegradable COD. This group is commonly observed to cover a

large number of compounds of different size and nature, and consequently, it is difficult to characterize the group by a single hydrolysis rate. This observation provides the basis of the recent approach to subdivide the slowly biodegradable COD into further fractions, namely rapidly hydrolysable COD (X_{SS}) and slowly hydrolysable COD (X_{SP}) (Henze, 1992).

Experimental evidence also indicates that the entire COD content of wastewaters cannot be removed through biological degradation, due to the presence of non-biodegradable or inert COD (C_I). The inert fraction is analysed in two subgroups of soluble inert COD (S_I) and particulate inert COD (X_I). These subgroups can also be defined as fractions of the total COD:

$$S_I = f_{SI}C_T$$

$$X_I = f_{XI}C_T$$

and

$$C_I = (f_{SI} + f_{XI})C_T = f_I C_T$$

where

f_{SI} = soluble inert fraction of the influent COD
 f_{XI} = particulate inert fraction of the influent COD

and

f_I = total inert fraction of the influent COD.

Experimental assessment of COD fractions

The readily biodegradable COD, S_S

The correct assessment of the readily biodegradable COD concentration (S_S) is important because this fraction is conceived as the rate limiting substrate component for heterotrophic growth. Methods used for its determination rely on respirometric measurements conducted under aerobic or anoxic conditions, in continuous or batch reactors. In the aerobic batch test adopted in this investigation, the selection of an appropriate initial F:M ratio provides a clear differentiation between oxygen utilization rates (OUR) induced by S_S and X_S . The initial OUR stays constant over a period where the maximum growth rate is sustained; after the depletion of S_S , it drops to a lower level only correlated with the hydrolysis of X_S and the

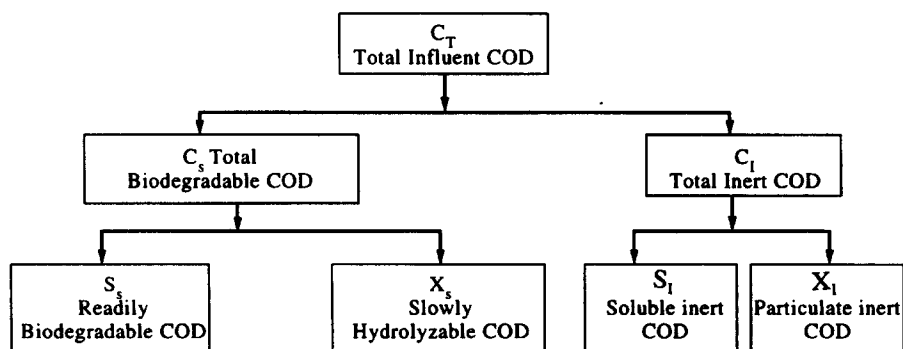


Fig. 6. Distribution of COD fraction in wastewaters.

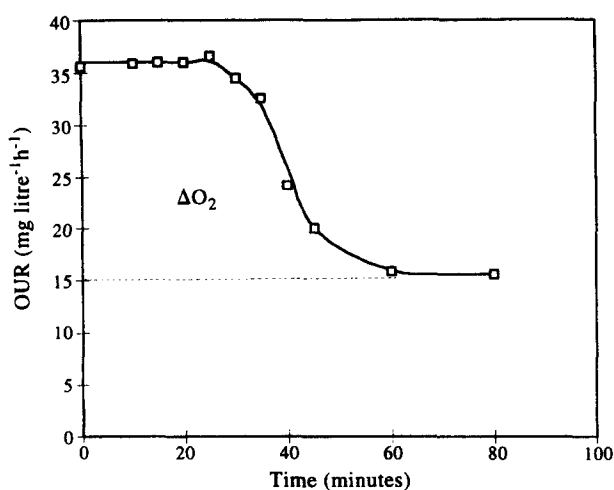


Fig. 7. Assessment of the readily biodegradable COD in domestic sewage (run no. 11).

endogenous respiration. The readily biodegradable substrate (S_S) may be calculated from the following relationship:

$$S_S = \frac{1}{1 - Y_H} \Delta O_2$$

where ΔO_2 is the difference between total respiration and respiration due to hydrolysed substrate and endogenous metabolism, and Y_H is the heterotrophic yield.

The experimental evaluation was carried out on 13 different samples from station 1 (Kadıköy). The mean COD concentration of the samples investigated was 605 mg litre⁻¹, a higher value than 410 mg litre⁻¹ previously ascertained as the mean COD content of the domestic sewage in Istanbul and corresponding to the 93.5 percentile of the COD distribution given in Fig. 2, and therefore a more representative value for practical evaluation and design. The initial F:M ratio chosen for the experiments varied in the range of 0.45–1.00, enabling clear identification of the oxygen uptake induced by the utilization of the readily biodegradable COD, as illustrated in Fig. 7, where ΔO_2 is depicted as

the area above the second OUR plateau presumably reached after the depletion of all readily biodegradable substrate of influent origin. In the experiments S_S was found to vary in the range of 23–86 mg litre⁻¹, with the majority of samples centred around 40–60 mg litre⁻¹, as outlined in Table 12. The mean S_S value was calculated as 54 mg litre⁻¹. Similarly, f_{SS} reflecting the $S_S:C_T$ mean ratio 0.09, varied in the range of 0.046–0.17, but for the bulk of the samples this range narrowed to 0.07–0.12. As indicated in Table 12, the mean S_S level constituted 29% of the total soluble COD fraction of domestic sewage.

The inert COD fraction and residual microbial products

Assessment of the inert COD fraction in sewage is quite important because it is an indirect indication of the other main biodegradable fraction, i.e. the substrate available for microbial growth. Inert COD components may be of influent origin or they may be generated as residual microbial products by means of growth or decay-associated processes (Daigger & Grady, 1977; Orhon *et al.*, 1989). Early methods proposed for the assessment of S_I have the major drawback of not differentiating soluble inerts from soluble residual fraction of microbial products, S_P (Ekama *et al.*, 1986; Henze *et al.*, 1987). Similarly, procedures for the assessment of X_I require that three other kinetic constants, namely the heterotrophic yield (Y_H), the endogenous decay rate (b_H), and the inert fraction of the biomass (f_{EX}), be correctly determined by independent methods and incorporated into the evaluation (Henze *et al.*, 1987). The method adopted in this study defines a new procedure enabling direct experimental determination of S_I and X_I (Orhon *et al.*, 1994a). It only relies on COD measurements and also identifies the soluble inert metabolic products (S_P) as a fraction of the total biodegradable COD in the influent (C_S):

$$S_P = Y_{SP} C_S$$

In this study, five different samples from station 1 (Kadıköy) representing a wide total COD range of

Table 12. Evaluation of experimental results for the readily biodegradable COD, (Sözen, 1995)

No. of sets	C_{T1} (mg litre ⁻¹)	S_{T1} (mg litre ⁻¹)	$X_{S1} + X_{I1}$ (mg litre ⁻¹)	S_{S1} (mg litre ⁻¹)	$S_{T1}:C_{T1}$	$S_{S1}:C_{T1}$	$S_{S1}:S_{T1}$
1	505	180	325	86	0.356	0.170	0.478
2	585	150	435	75	0.256	0.128	0.500
3	315	150	165	40	0.476	0.127	0.267
4	425	130	295	40	0.306	0.094	0.307
5	670	185	485	61	0.276	0.091	0.329
6	630	230	400	50	0.365	0.079	0.217
7	410	125	285	36	0.305	0.088	0.288
8	840	220	620	80	0.262	0.095	0.364
9	500	155	345	23	0.310	0.046	0.148
10	770	265	505	42	0.344	0.055	0.158
11	800	240	560	60	0.300	0.075	0.250
12	525	185	340	45	0.352	0.086	0.243
13	870	230	640	58	0.264	0.067	0.252
Mean	605	190	415	54	0.320	0.092	0.292

315–670 mg litre⁻¹ have been examined for their soluble and particulate inert COD contents. For the purpose of comparison, a sample from station 2 (Yenikapı), reflecting a mixture of domestic sewage and tannery effluents is also included in the evaluation. The results, as outlined in Table 13, yield a mean soluble inert fraction, f_{SI} , of 0.036 and a value of 0.10 for its particulate counterpart, f_{XI} . For a COD concentration of 450 mg litre⁻¹, which is the mean of the samples examined, the above fractions correspond to an S_I of 15 mg litre⁻¹ and an X_I of 44 mg litre⁻¹. For the sample from station 2, the f_{XI} fraction is, as expected, practically the same as the mean level characterizing the samples from station 1, while the f_{XI} fraction of 0.287, corresponding to an X_I value of 112 mg litre⁻¹, is substantially higher. This may be attributed to the fact that tannery effluents with high suspended solids content are occasionally dumped to the main collector which provided the sample.

Evaluation of results

The COD fractionation experiments yield meaningful results in terms of biological treatability of domestic sewage in Istanbul. Values for the major COD fractions are listed in Table 14, together with similar results reported for domestic wastewaters in different parts of the world. As shown in this table, the initial inert COD components total around 14%, so that only 86% of the total COD is of biodegradable nature. On the basis of a mean COD concentration of 410 mg litre⁻¹, the biodegradable fraction (C_S) amounts to 353 mg litre⁻¹. The readily biodegradable COD component is only 9% of C_T , finding its place in the lower part of the range of 7–32% reported in the literature for the same parameter. The relatively low value of 4% associated

with the soluble inert fraction of the Istanbul sewage is justifiable because it does not include, as in the other studies listed in Table 14, the soluble residual metabolic products. Together with these products, this fraction is calculated to go up to around 10%. The slowly biodegradable fraction resulting from the COD fractionation study is 77%, quite comparable with the levels given in the literature when the initial heterotrophic biomass (X_H) is also accounted for. Preliminary estimations show that X_H is also around 100 mg litre⁻¹ for the Istanbul sewage, but additional experiments are needed to confirm this value. A reliable estimation of this parameter is significant because it will also lead to the correct evaluation of the amount of available COD for biological treatment. Another significant point of interest is the fact that no default values can be set *a priori* for various COD fractions, as previously mentioned in significant modelling studies (Henze *et al.*, 1987; Orhon & Artan, 1994). These fractions, evaluated as significant components of current activated sludge models, are quite site-specific as evidenced by the data presented in Table 14 and should be experimentally identified for each study.

CONCLUSIONS

In the light of the experimental results summarized and evaluated in the preceding sections, the concluding remarks of this study may be expressed as follows.

Wastewater characterization was carried out at six different stations in the Metropolitan Area of Istanbul. The wastewater quality for stations 1, 2 and 3, collecting more than 50% of the wastewater generated in the

Table 13. Evaluation of experimental results for the inert COD fractions

No. of sets	C_{T1} (mg litre ⁻¹)	S_{I1} (mg litre ⁻¹)	X_{I1} (mg litre ⁻¹)	f_{SI}	Y_{SP}	f_{XI}
Station 1						
2	585	16	60	0.027		0.102
3	315	20	42	0.063		0.133
5	670	18	52	0.027		0.078
14	360	13	36	0.036	0.064	0.100
15	314	8.3	29.4	0.026	0.096	0.093
Mean	449	15	44	0.036		0.100
Station 2						
16	390	15	112	0.038	0.086	0.287

Table 14. COD fractionation of domestic wastewaters

	S_{I1} (%)	S_{S1} (%)	X_{S1} (%)	X_{H1} (%)	X_H (%)	Reference
South Africa	5	20	62	—	13	(Ekama <i>et al.</i> , 1986)
Switzerland	11	32	45	—	11	(Henze <i>et al.</i> , 1987)
Hungary	9	29	43	—	20	(Henze <i>et al.</i> , 1987)
Denmark I	8	24	49	—	19	(Henze <i>et al.</i> , 1987)
Denmark II	2	20	40	20	18	(Henze, 1992)
Switzerland I	20	11	53	7	9	(Kappeler & Gujer, 1992)
Switzerland II	10	7	60	15	8	(Kappeler & Gujer, 1992)
Switzerland III	12	8	55	15	10	(Kappeler & Gujer, 1992)
Turkey	4	9	77	— ^a	10	This study

^aIncluded in X_{S1} .

Metropolitan Area of Istanbul, was quite comparable and represented domestic sewage without appreciable impact of industrial discharges. The mean values of major parameters resulting from this evaluation can be given as 410 mg litre⁻¹ for COD, 180 mg litre⁻¹ for BOD₅, 210 mg litre⁻¹ for SS, 43 mg litre⁻¹ for TKN and 7.2 mg litre⁻¹ for total P. They show good agreement with unit loads of 40 g BOD₅ capita⁻¹ day⁻¹, 45 g SS capita⁻¹ day⁻¹, 6.7 g TKN capita⁻¹ day⁻¹ and 1.3 g total P capita⁻¹ day⁻¹, previously adopted for the assessment of the pollution load in the area, together with a unit wastewater flow rate of 160 litre capita⁻¹ day⁻¹.

The much stronger wastewater quality at the other stations can be explained on the basis of industrial interferences and water shortages in related areas. The results confirmed the common understanding that wastewater quality is very much site-specific and should be determined for each case.

Results of conventional characterization can be interpreted to yield, to a degree, a rough indication of the treatability of wastewaters. Size distribution of pollutants may be a significant index for physical and chemical treatment. In this context, the soluble COD fraction was observed to stay around 35% of the total COD, thus providing an indication that chemically assisted settling could provide more than 65% organic carbon removal.

The BOD₅:COD ratio, conventionally regarded as an index of biological treatability, was calculated as 0.47 for all stations depicting domestic sewage character and it was found to remain about the same for settled and soluble sewage fractions. Similarly, for the COD:N ratio, a parameter closely related to the denitrification potential, experimental results converged to a mean value of 9.2, practically the same as the limit below which predenitrification is favoured. In the settled and filtered wastewater portions, this parameter dropped to 6.5 and 3.6, very critical levels for effective nitrogen removal. These ratios reflect the delicate balance between the available carbon and nitrogen removal potential when pretreatment is incorporated prior to biological processes.

Biological treatability of the domestic sewage tested was best illustrated by COD fractionation, indicating that 14% of the wastewater COD was non-biodegradable. Of the remaining organic carbon content, only 10% was readily biodegradable and the bulk (77%) of the COD load was of slowly biodegradable nature, an observation quite in accordance with the findings previously reported in the literature for domestic wastewaters.

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